

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Characterization of metal-ligand bonding in lanthanide partitioning complexes	<b>Experiment number:</b> EV-5
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 10. 07. 2013 to: 16. 07. 2013	<b>Date of report:</b> 4.03.2014
<b>Shifts:</b> 18	<b>Local contact(s):</b> Jean-Daniel Cafun	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <sup>1)</sup> Tonya Vitova <sup>1), 3)</sup> Melissa Denecke <sup>2)</sup> Kristina Kvashnina <sup>1)</sup> Jörg Rothe <sup>1)</sup> Tim Prüßmann* <sup>1)</sup> Ivan Pidchenko* <sup>1)</sup> Andrea Kutzer* <sup>1)</sup> Karlsruhe Institut fuer Technologie (KIT); Institut fuer Nukleare Entsorgung (INE); P.O. Box 3640, D-76021 Karlsruhe, Germany <sup>2)</sup> European Synchrotron Radiation Facility (ESRF), 6 Rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France <sup>3)</sup> Dalton Nuclear Institute, The University of Manchester, Manchester, UK, M13 9PL		

## Report:

One of the major steps in the partitioning and transmutation (P&T) strategy for reduction the long-term radiotoxicity of spent nuclear fuel is the separation of 5f elements from their chemically similar 4f counterparts. This separation is necessary as some of the Ln(III) have large neutron cross sections and thereby compromise transmutation efficiency in the nuclear fission process. Selective liquid-liquid extraction of An(III) from Ln(III) has been demonstrated using soft donor extracting agents such as heterocyclic N-donor ligands: The hydrophobic bistriazinylpyridines (BTP) [1] and bistriazinylbipyridines (BTBP) [2] show excellent extraction efficiency, e.g., their separation factors (SF) for Am(III) over Eu(III) are higher than 100 ( $SF = D_{Am}/D_{Eu}$ ;  $D_M = [M]_{org}/[M]_{aq}$ ) upon extraction. Optimization of the partitioning ligands is a topic of global interest, as the present ligands do not yet fulfill all criteria for application in an industrial process. Such optimization implies basic understanding of the chemical and physical processes responsible for ligand selectivity for An(III) over Ln(III). Spectroscopic data available demonstrate thermodynamically favoured An(III) extraction from nitric acid solution into the organic phase over Ln(III). However, we found with extended X-ray absorption spectroscopy (EXAFS) only subtle structural differences between the An(III)-BTP and Ln(III)-BTP complexes in organic solution, which may not fully explain An(III)/Ln(III) selectivity [2, 3]. We performed Ln (Ln=Pr/Gd/Ho/Yb) L<sub>3</sub> edge high-energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) spectroscopy and core-to-core resonant inelastic X-ray scattering (CC-RIXS) measurements of Ln(NO<sub>3</sub>)<sub>3</sub> and Ln(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (CF<sub>3</sub>SO<sub>3</sub>=OTf) references and Ln(BTP), Ln(BTBP) and Ln(Bis-pyrazolylpyridine (BPP)) complexes by detecting the Ln L<sub>α1</sub> and L<sub>β2</sub> emission lines.

## Experimental details:

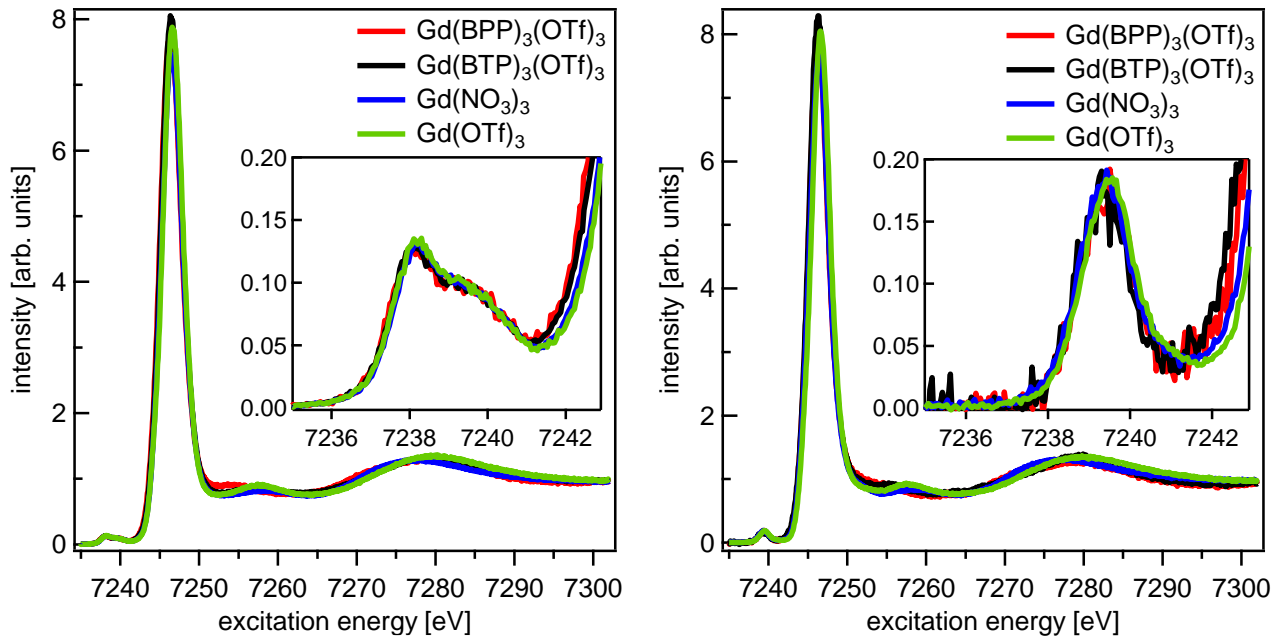
Ln(NO<sub>3</sub>)<sub>3</sub> and Ln(OTf)<sub>3</sub> (Ln=Pr/Gd/Ho/Yb) samples have been solved in isopropanol. N-propyl-bis-triazinylpyridine (BTP), C5-bis-pyrazolyl-pyridine (BPP) and C3-bis-triazinyl-bipyridines (BTBP) solutions in

isopropanol (BTP), octanol (BPP) and ethanol (BTBP) have been mixed in stoichiometric amount with  $\text{Ln}(\text{OTf})_3$  solution to form the complexes.  $\text{Ln}(\text{NO}_3)_3$  and  $\text{Ln}(\text{OTf})_3$  had concentrations of 10mmol/L, whereas the complexes ~5mmol/L. HERFD-XANES and CC-RIXS maps measurements of the samples were performed applying a five analyzer crystals spectrometer at the ID26 undulator beamline at ESRF. For the experiments the primary X-ray beam was monochromatized by a Si(311) double crystal monochromator. The emitted fluorescence was diffracted by five spherically bent crystals and focused on an avalanche photo diode. The different emission energies and corresponding crystals are shown in **Table 1**.

**Table 1:** Emission line energies and the corresponding spectrometer crystals for the measured Ln samples.

	emission energy [eV]	Crystal
Pr $\text{La}_1$	5033.0	Ge (331)
Pr $\text{L}\beta_2$	5849.4	Ge (333)
Gd $\text{La}_1$	6057.5	Si (333)
Gd $\text{L}\beta_2$	7101.8	Ge (620)
Ho $\text{La}_1$	6719.0	Si (440)
Ho $\text{L}\beta_2$	7909.1	Ge (444)
Yb $\text{La}_1$	7414.8	Ge (620)

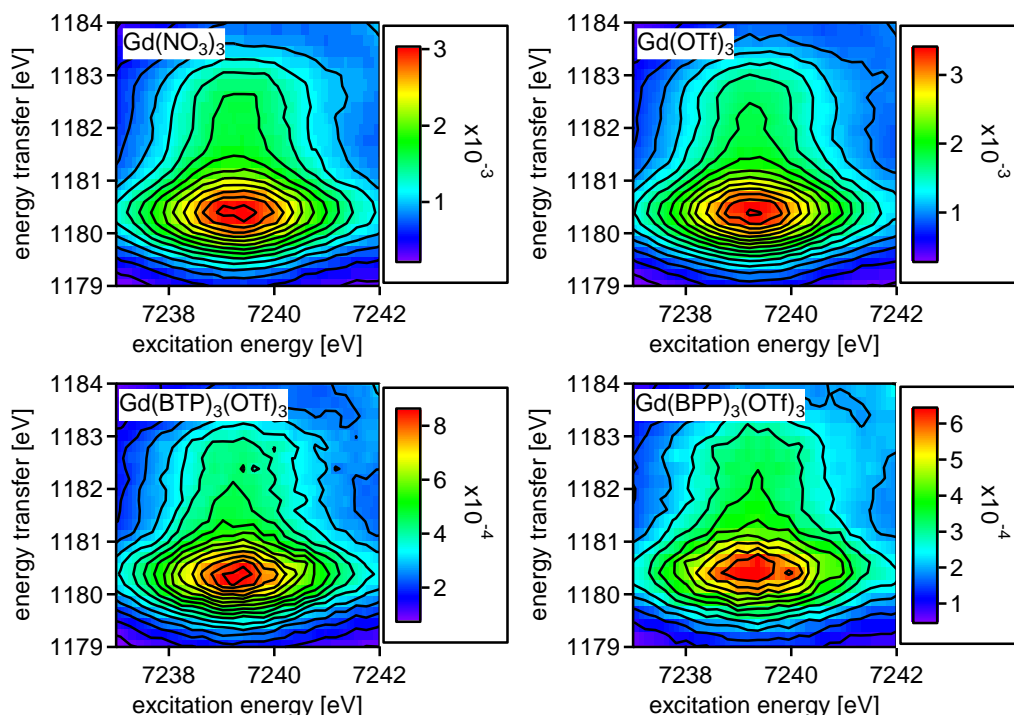
## Results and discussion:



**Figure 1:** Gd  $\text{L}_3$  edge HERFD-XANES spectra of  $\text{Gd}(\text{OTf})_3$ ,  $\text{Gd}(\text{NO}_3)_3$ ,  $\text{Gd}(\text{BTP})_3(\text{NO}_3)_3$  and  $\text{Gd}(\text{BPP})_3(\text{OTf})_3$  measured by recording the  $\text{La}_1$  (left) or the  $\text{L}\beta_2$  (right) emission lines.

One typical example of our studies is the Gd  $\text{L}_3$  edge HERFD-XANES spectra shown in **Figure 1** obtained by recording the  $\text{La}_1$  (left) and  $\text{L}\beta_2$  (right) emission lines, respectively. The spectra exhibit narrowing of the spectral features due to suppressed core-hole lifetime broadening effects [4-7]. In addition, a systematic energy shift of the white line (WL) of the complexes to lower energies is present. In the  $\text{L}\beta_2$  spectra the energy shifts are better resolved and present for all compounds. The relative energy shift of the WL for  $\text{Gd}(\text{BTP})_3(\text{OTf})_3$  and  $\text{Gd}(\text{BPP})_3(\text{OTf})_3$  over  $\text{Gd}(\text{OTf})_3$  and  $\text{Gd}(\text{NO}_3)_3$  are clear indications for better screening of the  $2p$  core-hole due to higher charge density on Gd in  $[\text{Gd}(\text{BTP})_3](\text{OTf})_3$  and  $[\text{Gd}(\text{BPP})_3](\text{OTf})_3$  compared to  $\text{Gd}(\text{OTf})_3$  and  $\text{Gd}(\text{NO}_3)_3$ . In both cases the pre-edge arising from excitations to  $4f$  states [7] shows no significant differences between the compounds. The origin of a single peak pre-edge in the  $\text{L}\beta_2$  spectra compared to a double peak in the  $\text{La}_1$  spectra is currently under investigation. The main difference in the

2p3d CC-RIXS maps describing the pre-edge region of these compounds (**Figure 2**) can be seen at 7241 eV excitation energy and 1183 eV energy transfer. The intensity relative to the pre-edge peak is higher for  $[\text{Gd}(\text{BTP})_3](\text{OTf})_3$  and  $[\text{Gd}(\text{BPP})_3](\text{OTf})_3$  compared to  $\text{Gd}(\text{OTf})_3$  and  $\text{Gd}(\text{NO}_3)_3$ . The effect is present mainly due to the shorter pre-edge – WL energy distance also observed in the XANES spectra.  $\text{L}_3$  edge spectra and CC-RIXS maps of Pr, Ho, Yb (not shown here) exhibit similar trends.



**Figure 2:** As measured 2p3d RIXS maps of  $\text{Gd}(\text{NO}_3)_3$ ,  $\text{Gd}(\text{OTf})_3$ ,  $\text{Gd}(\text{BTP})_3(\text{OTf})_3$  and  $\text{Gd}(\text{BPP})_3(\text{OTf})_3$ .

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## Acknowledgement:

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